

# SPECIFIC ACIDITY OF WATER EXTRACT AND OXALATE CONTENT OF FOLIAGE OF AFRICAN SORREL<sup>1</sup>

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(WITH ONE FIGURE)

## Foreword

This report is submitted, not so much as a contribution to the accumulated data on the composition of the leaves of *Rumex abyssinicus* Jacq., as for the purpose of directing the attention of food and drug analysts to a comparatively simple procedure by which much of value may be learned about the source of the acidity in certain acid materials, with the minimum expenditure of time and effort. The scheme outlined in this paper has already been applied by the writer to a study of dried apple pomace and pectin pulp, with gratifying results, and it is believed that it should prove of value in the study of other feeding stuffs of an acid character.

## Material examined

Among the plants brought to the United States for further study by the Office of Foreign Seed and Plant Introduction of the United States Department of Agriculture in 1919 was a native African sorrel, *Rumex abyssinicus* Jacquin.<sup>2</sup> The stock was brought from Angola, Portuguese West Africa, where the foliage is reported to be used as greens for human food. Dr. DAVID FAIRCHILD states as follows:

Preliminary trials at various points in this country have shown this species to possess distinct promise as a summer vegetable. By sufficient parboiling or boiling in a large amount of water, its acidity can be reduced to a point where it is distinctly agreeable, and since it is devoid of all stringiness it deserves to be widely known in America. The plant grows to a height of eight feet and produces an amazing amount of greens throughout the summer. It is as resistant to heat as New Zealand spinach and Swiss chard.

Dr. ARNO VIEHOEVER suggests caution, however, in the use of this material for food. The following statement by him<sup>3</sup> was written after the completion of the chemical work reported in this paper.

<sup>1</sup> From the Cattle Food and Grain Investigation Laboratory, Bureau of Chemistry, United States Department of Agriculture, Washington.

<sup>2</sup> S.P.I. no. 48023.

<sup>3</sup> Amer. Food Jour., January 1922.

The presence of considerable amounts of oxalic acid, as found in the Bureau of Chemistry, in the form of soluble oxalates, as well as calcium oxalate, suggests caution. It is a well known fact that some people are especially susceptible to poisoning from oxalic acid, and the poisoning cases reported after eating rhubarb leaves are by no means rare. It appears possible, however, that by the addition of calcium carbonate the soluble oxalates may be precipitated, and thus the major portion of the objectionable ingredient may be eliminated. Another means suggested, and possibly equally effective to make the product available for general consumption, would be the removal of the water in which the material has been soaked and boiled. At any rate, we have here a product which may be placed on the market, and which may be used as a substitute for spinach and other greens, but the identity and characteristics of which should be known to the consuming public and especially the food officials concerned with the welfare of the people.

Several plants started in the vicinity of Washington in 1920 made vigorous, healthy growth (fig. 1). Because of the promising character of the plant as a source of summer greens, it was decided to submit a sample to the Bureau of Chemistry for a determination of its oxalic acid content. The suggestion was made, however, that in order to decide the question of its wholesomeness it was essential that both the total (titrable) acidity and specific acidity (H-ion concentration) of a water extract of the material be determined, as well as the total oxalate content. These determinations were undertaken in conjunction with the colorimetric determination of specific acidity in certain feeding stuffs.

TABLE I  
DIMENSIONS OF LEAVES OF SAMPLES IN MM.

DIMENSION	SAMPLE NO. 38339			SAMPLE NO. 38340		
	Largest	Smallest	Average of 20	Largest	Smallest	Average of 11
Length of blade . . . . .	195	75	149.0	260	230	249
Extreme breadth of blade . .	150	45	118.0	250	200	220
Length of petiole . . . . .	120	40	86.5	140	100	125

On August 5, the plants in Washington being at a suitable stage of growth, a sample of about one pound of fresh foliage was analyzed. Practically all of the material obtained consisted of sound, crisp leaves with petioles. As there were two distinct sizes of leaves, the material was divided into two samples. The dimensions of the leaves constituting these samples are given in table I.



FIG. 1.—Row of plants of Abyssinian *Rumex*, about 6 feet high, grown at Yarrow Plant Introduction Garden near Rockville, Md. Photograph furnished by Office of Foreign Seed and Plant Introduction, Bureau of Plant Industry, U.S. Department of Agriculture.

## Procedure

### MOISTURE

The bulk of the material of each sample was used for the determination of moisture, but only entire leaves, with their petioles, were taken. After recording the total green weights, the midribs, larger veins, and petioles were split by a sharp knife to facilitate evaporation, and the material was rapidly dried at 65°–70° C. in a well ventilated oven, until friable. It was then crushed, care being taken to avoid loss of substance, and the samples finally dried to constant weight at 65°–70° C. in a vacuum oven. The loss in weight, about 90 per cent of the green weight, was taken to be total moisture. The dried material was ground and reserved for further study.

### TOTAL ACIDITY OF WATER EXTRACT

Several sound leaves with petioles, representative of the fresh green material, were selected from each sample, and the weights of the two charges recorded. In the case of the larger foliage two leaves, weighing 43 gm., constituted the charge, while several leaves, weighing in the aggregate 25 gm., represented the sample of smaller foliage. Each charge was thoroughly macerated in a glass mortar, and the resulting pulp transferred to a four-sided glass 8 oz. sample jar, with exactly 200 cc. of distilled water, previously boiled and cooled to room temperature. After violently stirring the mixture for 30 minutes by means of an electric mixer,<sup>4</sup> it was thrown on dry filter paper. The first (cloudy) portion of the filtrate was rejected, and the total acidity in an aliquot of the clear extract was determined by titrating with N/10 sodium hydroxide solution, using phenolphthalein as indicator. The presence in the water extract of a natural indicator,<sup>5</sup> the strongly darkening color of which tended to obscure the end-point of the titration, made it necessary to carry through concurrently a blank with a similar aliquot of extract with-

<sup>4</sup> Described in Circular 68, Office of the Secretary, U.S. Department of Agriculture.

<sup>5</sup> This natural dye in the leaves of *R. abyssinicus* Jacq. appears pink in dilute aqueous extracts of natural acidity. As titration with a fixed base progresses, the color changes through yellow to brown, at about the neutral point, and the solution becomes inky when made distinctly alkaline.

out phenolphthalein. In this blank titration, the addition of N/10 sodium hydroxide solution kept pace with the quantity added in the true titration, and the end-point was determined by contrasting the colors of the titrated extracts. The extract containing phenolphthalein developed a noticeably redder brown color than the other.

In the computations allowance was made for the water present in the green material. The total titrable acidity is expressed as cubic centimeters of normal acid per kilogram of leaf material, termed the "degree of acidity."

#### SPECIFIC ACIDITY OF WATER EXTRACT

The specific acidity was estimated on a portion of the clear extract by a slight modification of the colorimetric method described by GILLESPIE (3) after BARNETT and CHAPMAN (1), in which use is made of the principle introduced by CLARK and LUBS (2), following SALM (7), of "superimposing the two extreme colors of an indicator in determining its half-transformation point." Instead of using a system of nine pairs of tubes having drop ratios 1:9, 2:8, etc., MEDALIA'S (4) system of seven pairs, having  $P_H$  exponent intervals of 0.2 between each pair for the indicators used, was adopted. For convenience the procedure is briefly sketched here.

The color comparisons are made in the small "block" comparator described by GILLESPIE. Seven pairs of test-tubes, selected to fit the comparator and for their uniformity in bore, are calibrated for 5 cc. capacity and arranged in a double row test-tube rack. A total of eight drops of the suitable indicator solution is delivered into each pair of tubes, 1 to 7 drops in the front seven tubes and 7 to 1 drops in the back row, care being taken to hold the delivery pipette in an upright position. Sufficient alkali<sup>6</sup> (dilute acid in the case of the indicator thymol blue, acid range) is then added to the tubes in the front row to produce the full alkaline color, and sufficient acid to develop the full acid color is added to those in the rear row. The tubes are then carefully filled to the 5 cc. mark with distilled water, previously boiled and cooled. Similar tubes are used for the solutions under examination (the water extracts of the sorrel). Eight drops of the indicator solution are required, of course, and the

<sup>6</sup> Quantity of alkali or acid varies somewhat for the different indicators.

5 cc. volume is completed with the "unknown" solution. The contents of all tubes are well mixed before making the color comparisons. (Mixing may be accomplished by rolling the tube back and forth between the palms of the hands.)

In making the color comparisons, the tubes, held vertically in the comparator, are arranged in two files of three tubes each, one file being made up of the tube containing the "unknown," *with* indicator solution and two tubes of distilled water, and the other file consisting of a pair of the standard tubes and a tube containing the "unknown" solution, *without* indicator. This arrangement is necessary to obviate optical differences caused by thickness of liquid viewed on the one hand, and on the other to offset the natural color and any turbidity of the extract under examination. Different pairs of standards are tried until the color of light passing horizontally through that file of tubes matches the color from the file containing the tube of "unknown," *with* indicator.

As stated by GILLESPIE, the tubes are viewed best against the sky. Occasionally, in the case of certain indicators, such as bromphenol blue, trouble is experienced in matching the colors because of a dichroic effect, especially noticeable in turbid solutions. In such cases the tubes may be viewed by the yellow light of a carbon electric lamp, screened as advised by CLARK and LUBS. Only two indicator solutions were needed in estimating the specific acidity of the sorrel extracts, an 0.05 per cent aqueous solution of bromphenol blue,<sup>7</sup> and an 0.02 per cent solution of thymol blue (thymol-sulphonphthalein) in 80 per cent alcohol.

To develop the full acid and "alkaline" colors respectively, in the standard paired tubes, the following quantities of reagents were used for the two indicators:

*Bromphenol blue.*—To produce the acid color, 0.5 cc. of N/10 hydrochloric acid solution; to produce the alkaline color, 1 drop of N/20 sodium hydroxide solution.

*Thymol blue (acid range).*—To produce the full acid color, 2 cc. of 1.25 per cent hydrochloric acid solution; to produce the color of

<sup>7</sup> Tetrabromophenolsulphonphthalein. The 0.05 per cent solution was prepared by diluting one volume of the indicator solution, furnished in the LaMotte field set, to twenty volumes, with freshly boiled and cooled distilled water.

the "alkaline" end of the range, 1 cc. of 0.005 per cent (N/700) hydrochloric acid solution.

The volume in all the tubes should be made up at once to 5 cc. The specific acidity values accepted for the several drop ratios are given in table II. This specific acidity is based on the H-ion concentration of pure neutral water as unity, as defined by WHERRY (10). The articles by WHERRY and ADAMS (11) and CLARK (11) discuss this system of stating H-ion concentration.

TABLE II  
SPECIFIC ACIDITY VALUES IN ROUND NUMBERS

DROP RATIO	BROMPHENOL BLUE		THYMOL BLUE, ACID RANGE	
	Specific acidity	P <sub>H</sub>	Specific acidity	P <sub>H</sub>
1:7.....	6300	3.2	400,000	1.4
2:6.....	4000	3.4	250,000	1.6
3:5.....	2500	3.6	160,000	1.8
4:4.....	1600	3.8	100,000	2.0
5:3.....	1000	4.0	63,000	2.2
6:2.....	630	4.2	40,000	2.4
7:1.....	400	4.4	25,000	2.6

These specific acidity (and P<sub>H</sub>) values, while not absolutely exact, are close enough for the purposes of this investigation, particularly as it was found that the specific acidity of the sorrel extracts fell at the extreme acid end of the bromphenol blue series, or between that and the "alkaline" end of the thymol blue, acid range, where a close estimation is impossible.<sup>8</sup> The sorrel extracts, however, were checked up by comparison with the straight acid color of the first indicator and the straight "alkaline" end color of the thymol blue, acid range.

The color standards are quite permanent, and if the tubes are stoppered and kept in the dark they may be used over a long period (4). The literature citations, particularly 3 and 4, contain details on the use of indicators covering P<sub>H</sub> values from 1.2 to 9.8. Both titrable and specific acidity were determined also on water

<sup>8</sup> As stated by GILLESPIE, measurements cannot be accepted at the point where the drop ratio is 9:1 or 1:9 (7:1 or 1:7), as the percentage transformation of the indicator is so nearly 100 or zero that the H<sup>+</sup> exponent may be far from that represented by the ratio, and this would not be disclosed by a difference in color.

extracts of dried and ground material of both samples. All determinations were made at room temperature, 25°–30° C. The higher temperature was usually reached in the afternoon during August.

#### TOTAL OXALATE

The estimation of total oxalate was undertaken for the purpose of verifying the figures obtained in the acidity work, and a critical study of oxalate methods was not attempted. After the completion of this work, the writer's attention was directed to a method, perfected by W. F. KUNKE, Bureau of Chemistry, for the determination, with a high degree of accuracy, of the total oxalate content of plant material. Using this method on another sample of the sorrel foliage, KUNKE obtained materially lower figures than those reported in this paper for total oxalate. Because of this and the relative crudity of the usual method, the figures for total oxalate herein reported are probably somewhat high. This, however, in no way invalidates the data dependent on the acidity determinations (the figures for potassium binoxalate), as whatever error there may have been appears in the figures for calcium oxalate.

The total oxalate content was estimated only on the dried and ground material. Two gm. was weighed into a 150 cc. volumetric flask, about 100 cc. of 2 per cent hydrochloric acid solution added, and the mixture, after being heated to boiling, was digested for thirty minutes on the steam bath. After cooling and completing the volume to 150 cc. with distilled water and mixing, the extract was filtered through dry filter paper. The total oxalate in 100 cc. of the hydrochloric acid extract was estimated by precipitation with calcium chloride and titration of the oxalate with standard solution of potassium permanganate, in the usual way. Contamination of the calcium oxalate precipitate with organic matter necessitated double precipitation, and the final precipitate was washed with 1 per cent acetic acid solution in the cold, for further purification.<sup>9</sup> Two control determinations on pure sodium oxalate were conducted under the same conditions as those for the sorrel samples. In the titration, which was carried through rapidly, there appeared to be a

<sup>9</sup> Final precipitation of calcium oxalate in acetic acid solution would be preferable for a material of this nature.



definite end-point, at which the pink color of the permanganate persisted for an appreciable interval of time, although organic matter, small amounts of which undoubtedly were present, continued slowly to reduce additional permanganate.

### Results

The data obtained in the chemical examination of the fresh and dried sorrel leaves are given in tables III, IV, and V.

TABLE III  
ANALYSIS OF LEAVES OF *Rumex abyssinicus*

SAMPLE	PERCENTAGE MOISTURE AT 65°-70° C.	DEGREE OF ACIDITY (cc. normal acid per kg.)	PERCENTAGE TOTAL OXALATE AS (C <sub>2</sub> O <sub>4</sub> )*
Misc. Div. No. 38339, small leaves with petioles (fresh) . . . . .	90.77	152.7	1.69
Dried at 65°-70° C. and ground	2.99	1490.0†	17.8
Misc. Div. No. 38340, large leaves with petioles (fresh) . . . . .	89.59	185.4	1.73
Dried at 65°-70° C. and ground	2.50	1500.0†	16.2

\* As stated previously, according to KUNKE these figures may be somewhat high.

† Evidently there was a decrease in acidity during drying, for the degrees of acidity as determined on the dried material, computed to the original moisture bases, would be 141.8 and 160.2 respectively.

TABLE IV  
WATER EXTRACT OF LEAVES

SAMPLE	QUANTITY OF SAMPLE PER 100 CC. OF EXTRACT (gm.)	TOTAL ACIDITY IN 100 CC. OF EXTRACT EXPRESSED AS NORMAL ACID (cc.)	SPECIFIC ACIDITY, H-ION CONCENTRATION			
			Of water extract of <i>Rumex</i> leaves (observed)		Of aqueous solution of HKC <sub>2</sub> O <sub>4</sub> having same total acidity as water extract of <i>Rumex</i> leaves (computed)*	
			Specific acidity	P <sub>H</sub>	Specific acidity	P <sub>H</sub>
No. 38339, small leaves with petioles (fresh) . . . . .	11.26	1.72	6300-10,000	3.2-3.0	9000	3.05
Dried . . . . .	1.00	1.49	6300	3.2	8400	3.08
No. 38340, large leaves with petioles (fresh) . . . . .	18.07	3.35	10,000-16,000	3.0-2.8	12600	2.90
Dried . . . . .	1.00	1.50	6300	3.2	8400	3.08

\* The method of computation is discussed later under Discussion. Attention is directed to the close agreement between the observed values and those computed for a pure potassium binoxalate solution.

Table IV gives the figures relating to the acidity of water extracts of both the fresh and dried material, and specific acidity values computed for pure solutions of potassium binoxalate of the same respective normalities (titrable acidities) as the water extracts.

TABLE V  
PERCENTAGE OF OXALATES AND EQUIVALENTS IN LEAVES

Sample	$\text{HKC}_2\text{O}_4$ in leaves (based on acidity of water extract of dried material)	$(\text{C}_2\text{O}_4)$ equivalent of $\text{HKC}_2\text{O}_4$ in preceding column	Total $(\text{C}_2\text{O}_4)$ in leaves from table III	Total $(\text{C}_2\text{O}_4)$ minus acid $(\text{C}_2\text{O}_4)$ , column 4 minus column 3	Calcium oxalate $(\text{CaC}_2\text{O}_4)$ in leaves equivalent of $(\text{C}_2\text{O}_4)$ in preceding column
No. 38339, small leaves (fresh).....	1.82	1.25	1.69	0.44	0.64
Dried.....	19.09	13.10	17.80	4.70	6.80
No. 38340, large leaves (fresh).....	2.05	1.41	1.73	0.32	0.47
Dried.....	19.22	13.20	16.20	3.00	4.40

The data in table V are derived entirely from determinations made on the dried material. In the second and last columns the data from tables III and IV are correlated to show the percentage amounts of salts of oxalic acid presumably present in both the fresh and dried leaves. The percentages given for calcium oxalate are for the anhydrous salt, for convenience in comparing with data in pharmacological literature.

The assumption that most of the oxalate is present as potassium binoxalate and calcium oxalate (as the monohydrate) is substantiated by additional information obtained through the kindness of DR. WHERRY. The work of MR. DEUEL on total soluble oxalate also checks in a striking manner the figures for binoxalate.

#### CRYSTALLOGRAPHIC-OPTICAL EXAMINATION

WHERRY, who examined some of the dried and ground material by polarized light, under a petrographic microscope, identified numerous crystals of potassium binoxalate, and a smaller number of crystals of calcium oxalate monohydrate in groups. The potassium binoxalate crystals were readily identified, because of their characteristic of having a relatively low alpha index. WHERRY

states that four substances might conceivably be present in the sample of plant tissue, and first determined their optical properties as follows:

	Alpha	Beta	Gamma	2 E.	Sign
Oxalic acid dihydrate. . . . .	1.445	1.505	1.540	120°	—
Potassium binoxalate. . . . .	1.415	1.545	1.565	65°	—
Potassium oxalate monohydrate. . . . .	1.440	1.485	1.550	160°	+
Calcium oxalate monohydrate. . . . .	1.490	1.555	1.650	Over 180°	+

Examination of the sample showed two distinctly different crystalline substances to be present, one in rosettes of acute crystals, the other in nearly equant grains. The first proved to have the refractive indices characteristic of calcium oxalate as indicated, the second to have those of potassium binoxalate. The calcium salt occurs as aggregates of crystals, and therefore looks more prominent, but considering the large number of small grains of the potassium salt which are scattered around, it is evident that the potassium salt is present in the greater amount. Immersion liquids 1.490 and 1.565 are most suitable for distinguishing the two, the potassium salt having one index much lower than the first, the calcium salt one much greater than the second. As no crystals were found to be present with gamma less than 1.560, or beta less than 1.540, it is to be inferred that neither oxalic acid nor neutral potassium oxalate is present, at least in significant amounts.

#### TOTAL DISSOLVED OXALATES

DEUEL has kindly consented to the inclusion in this paper of figures obtained by him for the soluble oxalate in a sample of foliage from the same group of plants from which these samples were obtained. His procedure was to boil the finely minced leaves in water for 1.5 hours, filter, make up the extract to definite volume, and in an aliquot determine the total soluble oxalate gravimetrically by precipitation as calcium oxalate, and after ignition, weighing as calcium oxid. In the two samples of foliage examined he found oxalate equivalent to 2.06 and 1.96 per cent potassium binoxalate. The percentage of moisture on the samples was not reported, but the figures are for the fresh leaves.

### Discussion

Much may be learned about acid material of the same general type as the foliage of *Rumex* sp., merely from a determination of the total (or titrable) and the specific acidity of a water extract of it. By "same general type" is meant here acid material in which, as in the sorrel, the "acidity" is due almost entirely to forms of a single acid. If, in addition to total and specific acidity, the total amount of the acid radical present in the water extract and in the material itself be known, it is possible to draw fairly accurate conclusions as to the quantities of the several salts of that acid actually present, without making elaborate determinations of the several basic elements. Auxiliary use of the petrographic microscope may afford valuable qualitative substantiation of the conclusions.

In this investigation the mere determination of "degree of acidity" (total titrable acidity of the water extract) of the sorrel foliage meant little; the acidity might have been caused by the presence of free oxalic acid. Determination of the specific acidity (H-ion concentration), however, proved conclusively that the acidity of the water solution could not have been caused by the presence of the free acid; as for the normality involved, the specific acidity value of oxalic acid would have been approximately ten times<sup>10</sup> the values actually found. On the other hand, the agreement between the "specific acidity" values determined experimentally for the sorrel extracts and those computed for pure solutions of potassium binoxalate of the same normality is striking. These values for potassium binoxalate solutions were computed by the help of the formula: Percentage ionization =  $100\left(\sqrt{KV} - \frac{KV}{2}\right)$ ,<sup>11</sup>

<sup>10</sup> Computed from data reported by THOMAS (9) after OSTWALD (5). Oxalic acid of a dilution comparable with the water extract of sample No. 38339 ( $N \times 0.0172$ ) is highly dissociated, the percentage ionized being 88.4 at 25° C., according to THOMAS' table.

<sup>11</sup> By an evident typographical error this formula in THOMAS' article was incorrectly stated: "Per cent ionization =  $100\sqrt{KV} - \frac{KV}{2}$ ." The method of calculating the  $P_H$  value is here appended in more detail, using as an example the data for the potassium binoxalate solution corresponding to the extract of the larger leaves: Normal-

derived from OSTWALD'S dilution law, as explained in detail by THOMAS (9). In this formula  $V$  = the volume in liters, in which one gram molecular weight of the substance is dissolved, and  $K$  = the dissociation constant. The values used for  $K$  are those given in SCUDDER'S (8) tables, and are for  $25^{\circ}$  C.

The data from the acidity determinations, therefore, point to potassium binoxalate as the sole source of the acidity of the sorrel extracts, at least of those of the dried material. Furthermore, a calculation of the percentages of this salt present in the samples based on the titrable "acid" in the extracts of the dried leaves yields figures agreeing very closely with those obtained by DEUEL for the oxalate (as potassium binoxalate) dissolved by boiling water.

These data, per se, do not preclude the possibility of the presence in the foliage of approximately equivalent quantities of free oxalic acid and normal potassium oxalate, which would simulate the acid salt, and, in fact, in aqueous solution would be identical with it. WHERRY'S observations on the dried material decides the point beyond a doubt. The acid nature of the leaves is unquestionably due to the presence of potassium binoxalate.

On recalculating the figures obtained for titrable acidity in the dried material (on which are based the figures for potassium binoxalate in the leaves) to the original (green) moisture bases, it becomes apparent that there is a loss of titrable acid during the drying. These figures (footnote, table III) become 141.8 and 160.2 for "degrees of acidity" on the original bases, respectively equivalent to 1.82 and 2.05 per cent potassium binoxalate, while the acidity actually titrated in the fresh material yielded the figures 152.7 and 185.4 (in terms of potassium binoxalate corresponding to 1.96 and 2.38 per cent); therefore 10.9 and 25.2 cc. respectively of normal acid per kilogram of fresh leaves disappeared during the drying of the two samples. This lost "acid" may have been carbon dioxide or other weak volatile acids, or may be accounted for in part by changes in colloidal, acid-reacting protein. The discussion by

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ity of solution =  $0.0335 N$ ; hence  $V = 29.85$ ,  $K = 4.9 \times 10^{-5}$ . Percentage ionization =  $3.75\%$ .  $H$  per liter =  $0.0335 \times 1.008$  gm.  $H^+$  per liter =  $0.0375 \times 0.0335 \times 1.008 = 0.001267 = 1.267 \times 10^{-3}$ .  $\therefore P_H =$  algebraic sum of  $-3$ , and  $\log. 1.267 = -2.897$ . Omitting the negative sign,  $P_H = 2.9$  (specific acidity = 12670).

PFEFFER (6) of decrease in acidity in plant tissues (in life) and in sap, due to a rise in temperature (from 15° to 45°) and to exposure to sunlight, fully explains a loss in acidity of this magnitude, on drying fresh material in which the cells are still functioning.

From the figures obtained for total oxalate it becomes apparent that there is more oxalate present in the leaves than is accounted for by the potassium binoxalate. Further, this excess oxalate must be either insoluble or neutral in reaction if soluble. Again the crystallographic-optical examination made by WHERRY decides the point. The only normal oxalate found was the insoluble calcium salt. A recapitulation of analytical results is presented in table VI.

TABLE VI  
ANALYSIS OF LEAVES OF *Rumex abyssinicus*

Leaves	Percentage moisture at 65°-70° C.	Percentage potassium binoxalate (HKC <sub>2</sub> O <sub>4</sub> )	Percentage calcium oxalate monohydrate (CaC <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O)	Degree of acidity (cc. normal acid per kilo)
Smaller leaves (fresh).....	90.77	1.82	0.73	152.7
Larger leaves (fresh).....	89.59	2.05	0.53	185.4
Smaller leaves (after drying).	2.99	19.09	7.80	1490.0
Larger leaves (after drying).	2.50	19.22	4.98	1500.0

A discussion of the influence of such quantities of oxalate on the edibility of the sorrel foliage, or of the physiological effects following its use as food, is outside the scope of this paper.

### Summary

1. The study here reported of the acidity and oxalate content of the leaves of *Rumex abyssinicus* (an African sorrel) demonstrates the advantages of determining the specific acidity (H<sup>+</sup> concentration), as well as the total (titrable) acidity of a water extract of acid material of this nature.

2. This paper brings together descriptions of relatively simple procedures, worked out by the investigators cited, for (1) colorimetrically determining, without the use of buffer solutions, the specific acidity of such water extracts, and (2) computing, for purposes of comparison, the specific acidity and P<sub>H</sub> value of pure solutions of the acid substance suspected of being the source of the

acidity. Through a comparison of these values, matching the specific acidity actually determined against that computed for those substances causing the acidity, a means of identifying, or at least indicating, the principal source of the acidity is described.

3. The data indicate that only two compounds of oxalic acid, potassium binoxalate and calcium oxalate monohydrate, occur in the *Rumex* leaves examined. The percentages in which these salts occur are computed from the data for acidity and total oxalate in the dried material.

4. Attention is directed to the value of a crystallographic examination in corroborating the results of the chemical work. It is believed that the scheme of investigation described should prove of value to analysts in examining drugs, foods, or feeding stuffs of an acid character.

5. The presence of a natural indicator in the leaves of *R. abyssinicus*, the aqueous solutions of which are pink in the natural acid solution, is noted. On adding a fixed alkali the solution changes its color through yellow to brown, becoming nearly black when distinctly alkaline.

The writer wishes to thank Mr. PAUL G. RUSSELL of the Office of Foreign Seed and Plant Introduction for making examination of this material possible, for furnishing information as to the history of the plant and its culture in this locality, and for providing the fresh foliage for analysis. Also acknowledgment is due Messrs. DEUEL and KUNKE for their kindness in permitting the inclusion of notes of their work, and Dr. WHERRY for his helpful suggestions and for the crystallographic examination of the leaf material.

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